5-(Methylidene)barbituric acid as a new anchor unit for dye-sensitized solar cells (DSSC)

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This paper is dedicated to Professor Oleg N. Chupakhin on the occasion of his 80th birthday

DOI: http://dx.doi.org/10.3998/ark.5550190.p008.686

Abstract
Novel dyes bearing a 5-(methylidene)barbituric acid moiety as a new acceptor/anchor fragment were obtained and exhibited remarkable photophysical properties, according to a preliminary assessment of their sensitization activity as elements for dye-sensitized solar cells.

Keywords: Barbituric acid, carbazole, pyrimidine, anchor group, push-pull structure, dye-sensitized solar cells

Introduction

Dye-Sensitized Solar Cells (DSSCs)[1-4] based on organic dyes adsorbed on nanocrystalline semiconductor (e.g. TiO_2, SnO_2, ZnO) electrodes are considered to be promising electronic devices having a number of advantages, such as a high efficiency of solar light-to-electricity conversion, light weight, low cost and nontoxic manufacturing. The photochemical properties of a variety of organic sensitizers have been extensively investigated.[2,4] However, the design of new dye-sensitizers with a visible light absorption coupled to long-lived excited states is still very important for improving of DSSCs. Typically, the metal-free organic dyes consist of donor (**D**) and acceptor/anchor (**A**) moieties connected with a π-bridge system, forming a so-called push–pull structure. Due to this structure of dye molecules, intramolecular electron-charge transfer takes place on absorption of light (Figure 1).

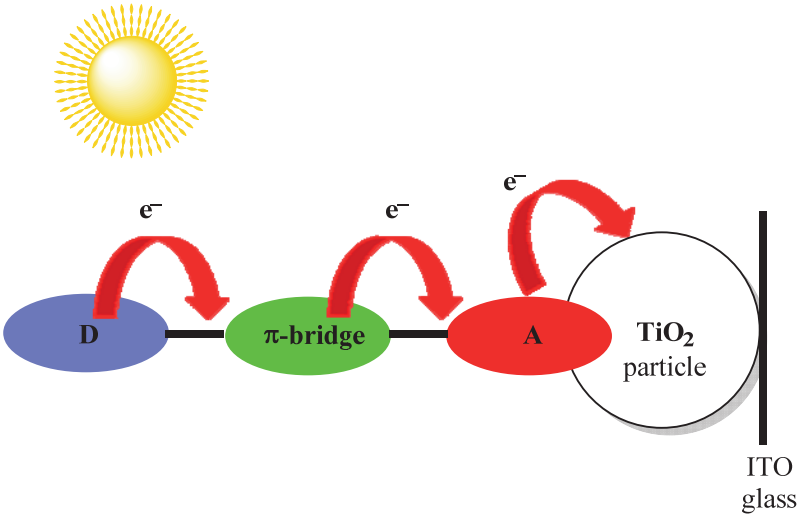
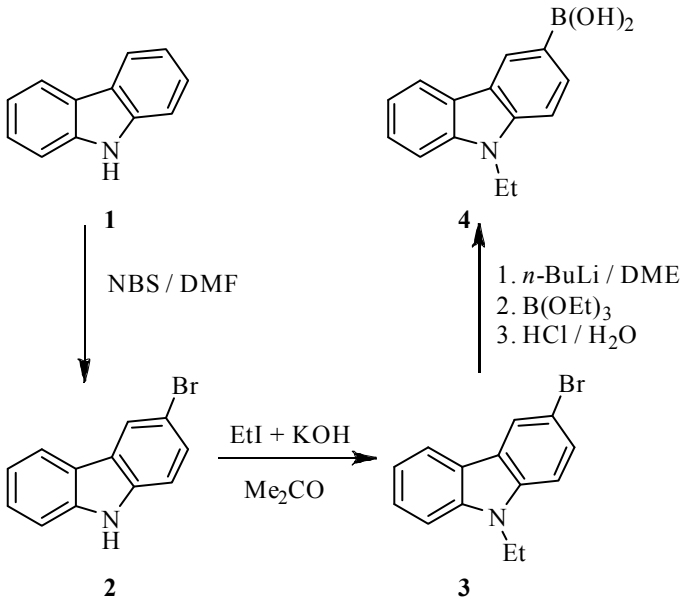


Figure 1. The diagramatic structure of a push-pull organic dye-sensitizer.

It should be noted that the acceptor moiety of a dye-sensitizer has a significant influence for electron-transfer processes and optical absorption of the dye. Besides that, it serves for anchoring of dye molecules onto the semiconductor surface. In contrast to a diversity of electron-donating groups and π-bridges for effective sensitizers, a limited number of acceptors have been reported in the literature. One of the commonly used acceptor/anchor moieties is 2-cyanoacrylic acid.[5-7] In this connection the development of novel acceptors/anchors for dye-sensitizers is a very crucial task to enhance performance of DSSCs.

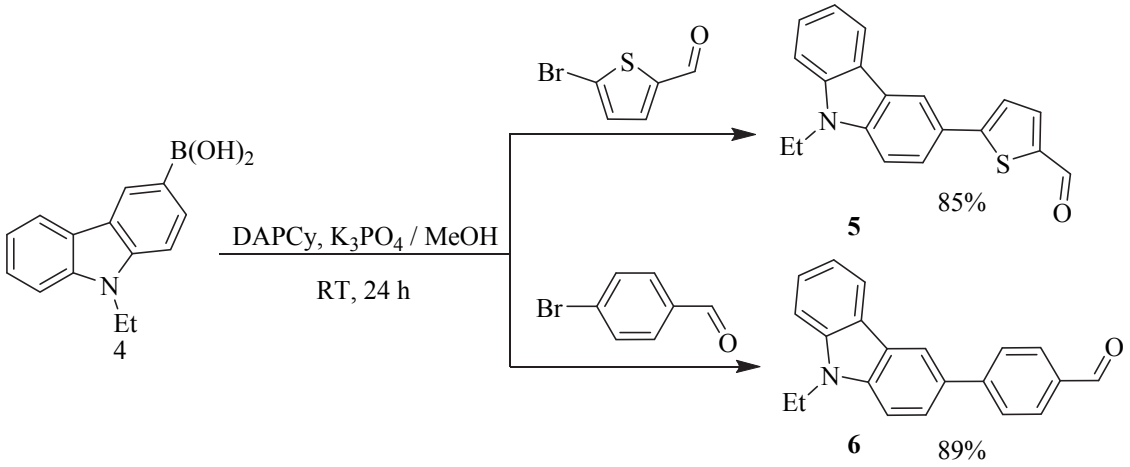
Results and Discussion

In this paper we report the synthesis of two novel dyes bearing a 5-(methylidene)barbituric acid fragment, as a new acceptor/anchor group, and a carbazole unit, as a donor, which has recently been used successfully for the design of efficient dye-sensitizers.[8-10] Moreover, two novel related sensitizers with 2-cyanoacrylic acid, as a classical acceptor/anchor group, were prepared for comparison of their properties. Thus, the carbazol-3-ylboronic acid **4** was obtained from 3-bromocarbazole **3** according to a slightly modified literature procedure.[11] The brominated compound **3** was prepared by using successive bromination with *N*-bromosuccinimide (NBS) and standard N-alkylation procedures from carbazole **1** (Scheme 1).[12]



Scheme 1. Preparation of carbazol-3-ylboronic acid **4.**

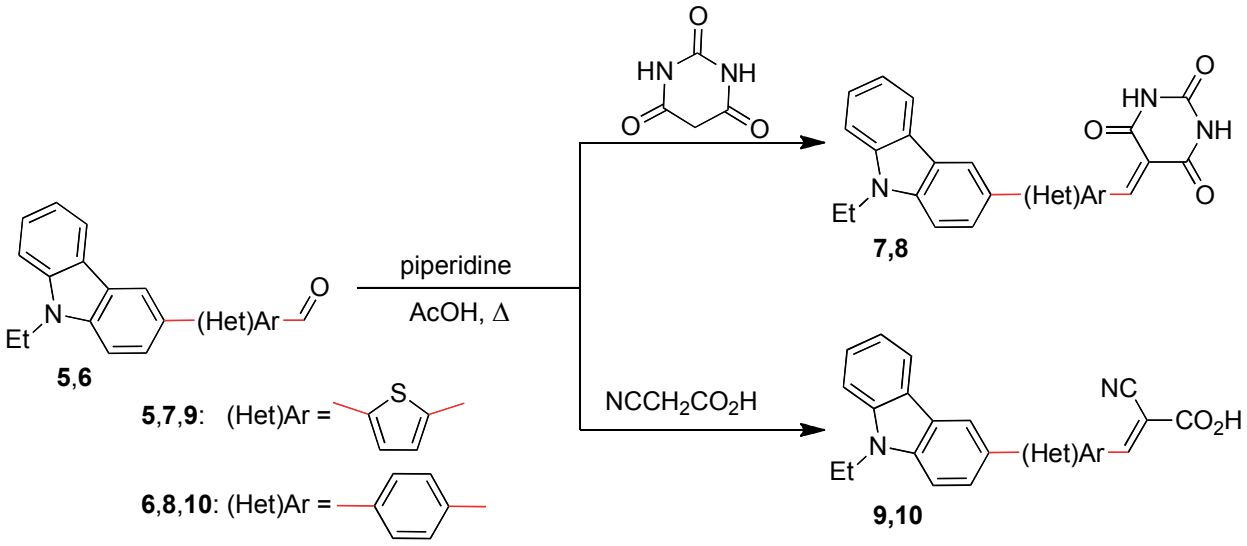
The aromatic aldehydes **5**,**6** bearing the carbazole unit were obtained in high yields using the Suzuki reaction between boronic acid **4** and 5-bromothiophene-2-carbaldehyde or 4-bromo-benzaldehyde, respectively. These cross-coupling reactions were carried out at ambient temperature in air for 24 hours, with 2 mol% *trans*-bis(dicyclohexylamine)palladium(II) acetate (DAPCy)[13] as the catalyst (Scheme 2).



Scheme 2. Preparation of aldehydes **5**,**6.**

The aldehydes **5** and **6** were used for the synthesis of push-pull dyes, as building-blocks containing the carbazole unit. Novel dyes **7**,**8** were obtained easily in excellent yields (compound **7**, 96%; compound **8**, 91%) by using the Knoevenagel condensation of aldehydes **5**,**6** with barbituric acid in glacial acetic acid under catalysis with piperidine at reflux for 5 hours. In a

similar way, dyes **9**,**10** were prepared in good yields under the same reaction conditions, starting from appropriate aldehydes and 2-cyanoacetic acid (compound **9**, 81%; compound **10**, 74%) (Scheme 3). It should be noted that incorporation of the fragments of 5-(methylidene)barbituric and 2-cyanoacrylic acids into the structure of dyes, as acceptor/anchor groups proceeded very smoothly.



Scheme 3. Synthesis of dyes **7**-**10.**

The UV-visible absorption spectra of dyes **7-10** in ethanol solution (2×10^{-5} mol/L) and adsorbed on TiO_2 nanoparticles were recorded at ambient temperature (Figure 2 and 3). Adsorption of these dyes on a TiO_2 surface was carried out from their THF solutions (2×10^{-5} mol/L) at ambient temperature for 24 hours. Samples of TiO_2 coated with the dyes were washed with ethanol and dried at 120 °C under vacuum.

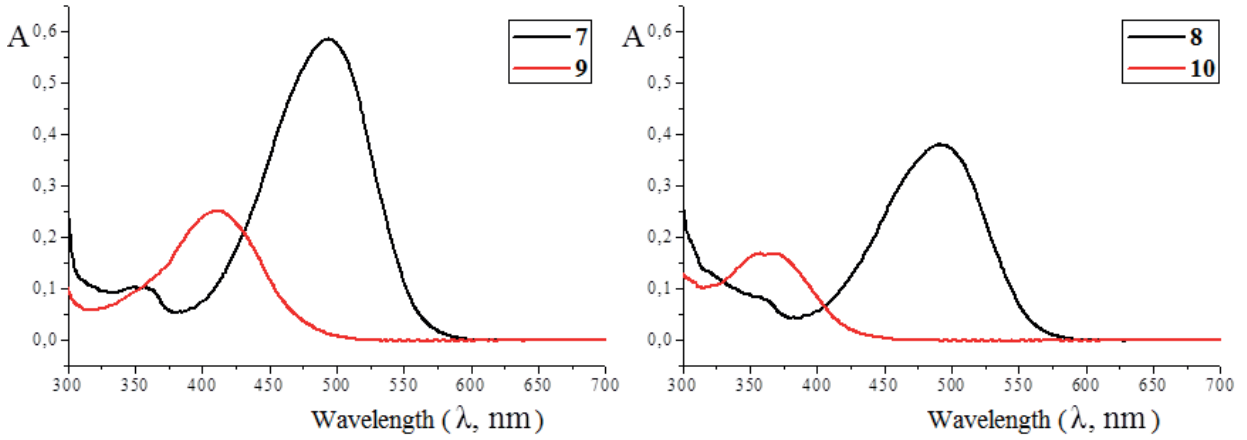


Figure 2. UV-vis spectra of dyes **7**,**9** and **8**,**10** in EtOH solution (2×10^{-5} mol/L).

The UV-spectra of dyes demonstrate maximum absorption wavelengths (λ_{max}) at 493 nm for **7**, 489 nm for **8**, 411 nm for **9**, and 362 nm for **10** (Figure 2). These peaks are ascribed to the intramolecular charge transfer from the electron-donating parts in these molecules to their acceptor fragments. The corresponding maximum molar extinction coefficients (ε) for dyes **7-10** are 2.92×10^4, 1.89×10^4, 1.25×10^4, and 0.84×10^4 $Lmol^{-1}cm^{-1}$, respectively. The red-shifts of the absorption band for 5-(methylidene)barbituric dyes **7**,**8** are approximately 90–120 nm in comparison to 2-cyanoacrylic dyes **9**,**10**, respectively. This trend continued after the dyes were anchoring on a TiO_2 surface, and λ_{max} for dyes **7-10** were 531, 495, 426 and 418 nm, respectively (Figure 3). Compared to the spectrum in ethanol solution, a slight red-shift and broadening of the absorption peak was observed for all dyes on a TiO_2 surface, which can be attributed to the formation of J-type aggregates.[14] These results show that 5-(methylidene)barbituric acid unit exhibits a stronger acceptor ability in the dye, thus increasing intramolecular charge transfer, and leading to the red-shift of absorption maximum with enhancement of molar extinction. It should be noted that the maximal visible light absorption is one of the most important characteristics of a dye-sensitizer for DSSC.

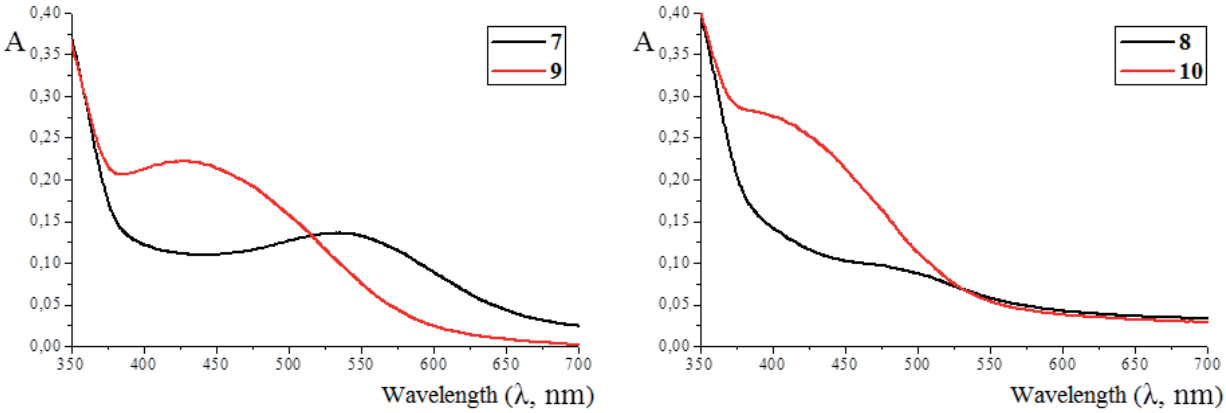


Figure 3. UV-vis spectra of dyes **7**,**9** and **8**,**10** anchoring on TiO_2.

Conclusions

We have obtained two novel dyes bearing a 5-(methylidene)barbituric acid fragment, as acceptor/anchor group, which have better characteristics for absorbtion visible light in comparison with those of the related dyes containing a 2-cyanoacrylic acid fragment (according to the maximum absorption wavelengths and corresponding molar extinction coefficients (ε) in their UV-spectra). In this respect, the 5-(methylidene)barbituric acid fragment is a new, promising acceptor/anchor unit for the design and further studies of novel dye-sensitizers for solar cell applications.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were obtained on Bruker DRX-400 and AVANCE-500 spectrometers with TMS as the internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. Melting points were determined on Boetius combined heating stages and are not corrected. IR spectra of samples (solid powders) were recorded on a Spectrum One Fourier transform IR spectrometer (Perkin Elmer) equipped with a diffuse reflectance attachment (DRA). Spectrum processing and band intensity determination were carried out using the special software supplied with the spectrometer. UV-visible spectra were recorded for a 2×10^{-5} M EtOH solution with Shimadzu UV-2401PC spectrophotometer (Diffuse Reflection with Shimadzu integrating sphere for solid samples).

General procedure for the preparation of aldehydes 5,6. K_3PO_4 (890 mg, 4.2 mmol) was added to a solution of 5-bromothiophene-2-carbaldehyde (270 mg, 1.4 mmol) or 4-bromobenzaldehyde (260 mg, 1.4 mmol), (9-ethylcarbazol-3-yl)boronic acid **4** (360 mg, 1.5 mmol) and *trans*-bis(dicyclohexylamine)palladium(II) acetate (16 mg, 0.028 mmol, 2 mol%) in MeOH (15 mL). The resulting suspension was stirred at ambient temperature for 24 h. MeOH was evaporated under vacuum and the residue was suspended in CH_2Cl_2 (20 mL), filtered from inorganic salts and concentrated under vacuum. The resulting residue was purified by flash chromatography of silica gel with $CHCl_3$/*n*-hexane (1:1) to remove by-products and then with EtOAc to give the appropriate aldehyde, **5** or **6**.

5-(9-Ethyl-9*H*-carbazol-3-yl)thiophene-2-carbaldehyde (5). Orange needles, yield 365 mg (85%), mp 145-6 °C (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H, C<u>H</u>O), 8.40 (d, *J* 1.7 Hz, 1H), 8.14 (d, *J* 7.7 Hz, 1H), 7.78 (dd, *J* 8.5, 1.9 Hz, 1H), 7.75 (d, *J* 3.9 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.46 – 7.41 (m, 3H), 7.30 – 7.26 (m, 1H), 4.38 (q, *J* 7.3 Hz, 2H, C<u>H</u>$_2$), 1.46 (t, *J* 7.3 Hz, 3H, C<u>H</u>$_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (s, 1H, C<u>H</u>O), 8.68 (d, *J* 1.6 Hz, 1H), 8.29 (d, *J* 7.7 Hz, 1H), 8.06 (d, *J* 4.0 Hz, 1H), 7.91 (dd, *J* 8.6, 1.7 Hz, 1H), 7.79 (d, *J* 4.0 Hz, 1H), 7.72 (d, *J* 8.6 Hz, 1H), 7.66 (d, *J* 8.2 Hz, 1H), 7.51 (t, *J* 7.7 Hz, 1H), 7.26 (t, *J* 7.4 Hz, 1H), 4.48 (q, *J* 7.1 Hz, 2H, C<u>H</u>$_2$), 1.34 (t, *J* 7.1 Hz, 3H, C<u>H</u>$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.6, 156.3, 141.2, 140.5, 137.8, 126.4, 124.4, 124.1, 122.9, 122.7, 120.7, 119.6, 118.6, 109.0, 108.9, 37.8, 13.8; IR(DRA): 416, 504, 551, 583, 625, 663, 725, 742, 789, 867, 917, 1066, 1054, 1155, 1126, 1231, 1271, 1345, 1382, 1431, 1474, 1523, 1597, 1628, 1657, 1733, 1869, 2797, 2969, 3059 cm^{-1}; Anal. Calcd for $C_{19}H_{15}NOS$: C, 74.73; H, 4.95; N, 4.59. Found: C, 74.34; H, 4.92; N, 4.94.

4-(9-Ethyl-9*H*-carbazol-3-yl)benzaldehyde (6). Colourless crystals, yield 375 (89%), mp 152-3 °C (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H, C<u>H</u>O), 8.38 (d, *J* 1.4 Hz, 1H), 8.16 (d, *J* 7.8 Hz, 1H), 7.97 (d, *J* 8.4 Hz, 2H), 7.88 (d, *J* 8.3 Hz, 2H), 7.76 (dd, *J* 8.5, 1.8 Hz, 1H), 7.59 – 7.38 (m, 3H), 7.30 – 7.25 (m, 1H), 4.40 (q, *J* 7.2 Hz, 2H, C<u>H</u>$_2$), 1.47 (t, *J* 7.2 Hz, 3H, C<u>H</u>$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 148.27, 140.5, 140.1, 134.5, 130.6, 130.4, 127.6, 126.2, 125.2, 123.7, 123.0, 120.6, 119.4, 119.3, 109.0, 108.8, 37.7, 13.9; IR(DRA): 521, 689, 737, 757, 802, 836, 905, 942, 1024, 1084, 1126, 1168, 1213, 1235, 1282, 1306, 1333, 1379, 1449, 1475, 1594,

1688, 2743, 2838, 2978, 3054 cm^{-1}; Anal. Calcd for $C_{21}H_{17}NO\times0.05CH_3CO_2C_2H_5$: C, 83.82; H, 5.77; N, 4.61. Found: C, 83.74; H, 5.62; N, 4.76.

General procedure for the preparation of dyes 7-10. The appropriate aldehyde **5** (153 mg, 0.5 mmol) or **6** (150 mg, 0.5 mmol) and barbituric acid (128 mg, 1 mmol) or 2-cyanoacetic acid (85 mg, 1 mmol) were added to glacial acetic acid (10 mL) and the suspension was warmed to obtain a clear solution. Piperidine (170 mg, 0.2 mL, 2 mmol) was added and the reaction mixture was stirred at 120 °C for 5 h. The precipitate of product was filtered off and washed with MeOH (5×5 mL) and then dried at 100 °C to give a pure appropriate dye, **7-10**.

5-{[5-(9-Ethyl-9*H*-carbazol-3-yl)thiophen-2-yl]methylene}pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (7). Dark-red powder, yield 200 mg (97%), mp 242-1 °C (AcOH); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.26 (s, 1H, NH), 11.24 (s, 1H, NH), 8.70 (d, *J* 1.6 Hz, 1H), 8.51 (s, 1H), 8.33 (d, *J* 7.7 Hz, 1H), 8.22 (d, *J* 4.2 Hz, 1H), 7.96 (dd, *J* 8.6, 1.7 Hz, 1H), 7.86 (d, *J* 4.1 Hz, 1H), 7.74 (d, *J* 8.6 Hz, 1H), 7.66 (d, *J* 8.3 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.27 (t, *J* 7.4 Hz, 1H), 4.49 (q, *J* 7.0 Hz, 2H, CH_2), 1.34 (t, *J* 7.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.6, 163.2, 160.6, 150.3, 147.9, 145.7, 140.4, 140.1, 134.4, 126.5, 124.4, 124.1, 123.8, 122.9, 122.1, 120.9, 119.5, 118.6, 110.0, 109.5, 109.4, 37.2, 13.7; IR(DRA): 463, 525, 509, 552, 622, 750, 729, 797, 855, 967, 1086, 1124, 1155, 1191, 1235, 1297, 1258, 1347, 1393, 1448, 1471, 1506, 1544, 1595, 1657, 1692, 1734, 1942, 2171, 2830, 2974, 3058, 3188, 3410 cm^{-1}; Anal. Calcd for $C_{23}H_{17}N_3O_3S\times0.5H_2O$: C, 65.08; H, 4.27; N, 9.90. Found: C, 65.15; H, 4.02; N, 9.87.

5-[4-(9-Ethyl-9*H*-carbazol-3-yl)benzylidene]pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (8). Red powder, yield 185 mg (91%), mp 211-2 °C (AcOH); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.39 (s, 1H, NH), 11.26 (s, 1H, NH), 8.69 (d, *J* 1.5 Hz, 1H), 8.37 – 8.32 (m, 3H), 8.29 (d, *J* 7.7 Hz, 1H), 7.97 (d, *J* 8.6 Hz, 2H), 7.94 (dd, *J* 8.6, 1.7 Hz, 1H), 7.73 (d, *J* 8.6 Hz, 1H), 7.65 (d, *J* 8.2 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.25 (t, *J* 7.4 Hz, 1H), 4.49 (q, *J* 7.1 Hz, 2H, CH_2), 1.35 (t, *J* 7.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO) δ 163.6, 161.9, 154.5, 150.17, 145.1, 140.1, 139.8, 134.9, 130.5, 129.4, 126.1, 125.9, 124.8, 122.94, 122.4, 120.7, 119.1, 119.0, 117.8, 109.7, 109.3, 37.1, 13.7; IR(DRA): 461, 510, 531, 551, 569, 632, 664, 707, 723, 744, 796, 840, 941, 967, 1055, 1079, 1121, 1134, 1158, 1190, 1234, 1261, 1305, 1346, 1396, 1442, 1477, 1529, 1593, 1669, 1730, 2868, 2973, 3063, 3185 cm^{-1}; Anal. Calcd for $C_{25}H_{19}N_3O_3\times0.2H_2O$: C, 72.70; H, 4.73; N, 10.17. Found: C, 72.68; H, 4.49; N, 10.24.

2-Cyano-3-[5-(9-ethyl-9*H*-carbazol-3-yl)thiophen-2-yl]acrylic acid (9). Red powder, yield 150 mg (81%), mp 195-6 °C (AcOH); ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.66 (br.s, 1H, CO_2H), 8.65 (d, *J* 1.7 Hz, 1H), 8.50 (s, 1H), 8.31 (d, *J* 7.7 Hz, 1H), 8.05 (d, *J* 4.1 Hz, 1H), 7.88 (dd, *J* 8.6, 1.8 Hz, 1H), 7.81 (d, *J* 4.0 Hz, 1H), 7.72 (d, *J* 8.6 Hz, 1H), 7.66 (d, *J* 8.2 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.26 (t, *J* 7.4 Hz, 1H), 4.48 (q, *J* 7.1 Hz, 2H, CH_2), 1.34 (t, *J* 7.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.84, 155.28, 146.69, 141.86, 140.23, 140.15, 133.23, 126.47, 124.34, 123.84, 123.29, 122.86, 122.05, 120.93, 119.43, 118.48, 116.67, 110.00, 109.53, 96.78, 37.16, 13.69; IR(DRA): 460, 513, 533, 550, 573, 589, 629, 654, 722, 729, 752, 797, 818, 894, 930, 972, 1065, 1023, 1125, 1089, 1157, 1272, 1293, 1350, 1390, 1433, 1471, 1492, 1506, 1577,

1627, 1663, 1687, 2219, 2508, 2543, 2597, 2815, 2965, 3062, 3088 cm^{-1}; Anal. Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.95; H, 4.33; N, 7.52. Found: C, 70.82; H, 4.35; N, 7.65.

2-Cyano-3-[4-(9-ethyl-9*H*-carbazol-3-yl)phenyl]acrylic acid (10). Orange powder, yield 135 mg (74%), mp 190-1 °C (AcOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.93 (s, 1H, $CO_2\underline{H}$), 8.68 (s, 1H), 8.39 (s, 1H), 8.28 (d, *J* 7.7 Hz, 1H), 8.18 (d, *J* 8.4 Hz, 2H), 8.06 (d, *J* 8.4 Hz, 2H), 7.93 (d, *J* 8.6 Hz, 1H), 7.74 (d, *J* 8.6 Hz, 1H), 7.65 (d, *J* 8.2 Hz, 1H), 7.50 (t, *J* 7.5 Hz, 1H), 7.25 (t, *J* 7.5 Hz, 1H), 4.49 (q, *J* 7.1 Hz, 2H, $C\underline{H}_2$), 1.34 (t, *J* 7.1 Hz, 3H, $C\underline{H}_3$); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.48, 153.88, 145.57, 140.05, 139.77, 131.49, 129.39, 129.15, 126.94, 126.10, 124.78, 122.93, 122.35, 120.67, 119.09, 119.06, 116.41, 109.67, 109.34, 102.16, 37.07, 13.67; IR(DRA): 459, 517, 552, 580, 615, 626, 671, 726, 748, 766, 786, 798, 846, 894, 946, 1022, 1064, 1085, 1123, 1132, 1155, 1190, 1234, 1294, 1348, 1384, 1428, 1476, 1492, 1515, 1546, 1569, 1629, 1697, 2223, 2548, 2618, 2676, 2816, 2971, 3054 cm^{-1}; Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.32; H, 4.92; N, 7.49.

Acknowledgments

This work was supported by the Ural Division of the Russian Academy of Sciences (Grants № 12-P-3-1014, 12-P-3-1030, 12-T-3-1025 and 12-T-3-1031), the Russian Foundation for Basic Research (research projects No. 13-03-12434-ofi_m2, 13-03-96049-r_ural_a, 14-03-01017_A, 14-03-00479_A**)**, and the Scientific Council of the President of the Russian Federation (grant MK-3043.2014.3).

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